PROTOCOL FOR APPROVAL OF ALTERNATE TEST PROCEDURES FOR INORGANIC AND ORGANIC ANALYTES IN NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM MONITORING

Revision 1.3

January, 1996

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Cincinnati, Ohio 45268

PROTOCOL FOR APPROVAL OF ALTERNATE TEST PROCEDURES FOR INORGANIC AND ORGANIC ANALYTES IN NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM MONITORING

INTRODUCTION

An alternate test procedure (ATP) is one that differs from a method previously approved by the U. S. Environmental Protection Agency (USEPA) for determining the constituent of interest in National Pollutant Discharge Elimination System (NPDES) monitoring. Any person may apply for approval of the use of an alternate test procedure for a specific constituent in NPDES monitoring.

Before submitting an ATP application, however, the applicant is responsible for performing an in-depth comparison of the description of the proposed method with the description of the appropriate approved NPDES method(s), listed in Tables 1B, 1C, or 1D of section 136 of Title 40 of the Code of Federal Regulations (CFR). In this comparison each of the topics, outlined in the Method Description Requirements (pp. 2-4), must be considered in detail. If this comparison reveals that there are absolutely no differences in the technical details of the proposed and approved methods, the methods are considered identical and an ATP application is not required. If the proposed method differs slightly in any of the technical details, the applicant may choose to: (1) modify the method so that it is identical to one of the previously approved methods, (2) submit a simple 2-column comparison (see the text on p. 4 in the Method Description Requirements) for NERL-Cincinnati determination of the comparability of the proposed method or the need for an ATP application, or (3) submit an application for approval of an ATP.

Every ATP application shall be made by letter in triplicate. An application for nationwide (NW) approval of a proposed ATP should be forwarded to the Acting Director, Ecological Exposure Research Division - Cincinnati (NERL-Cincinnati), U.S. Environmental Protection Agency, Cincinnati, Ohio 45268. An application for approval of the limited-use (LU) of an ATP by a regional EPA laboratory should be forwarded directly to the appropriate Regional Administrator. An application for approval of the limited-use of an ATP by a State or commercial laboratory or an individual discharger or permittee shall be forwarded directly to the Director of the State Agency issuing NPDES permits in that State if that State has primacy (i.e., the state permit program is USEPA-approved). If the State does not have primacy, then the application by a State or commercial laboratory or individual discharger or permittee

should be forwarded directly to the appropriate USEPA Regional Administrator. The State Agency Director and USEPA Regional Administrator will forward applications as required.

APPLICATION REQUIREMENTS

The general requirements for an ATP application include the name and address of the applicant and/or authorized representative; if applicable, the applicant's NPDES permit number; the pollutant or constituent for which the ATP is proposed; the type of approval desired (NW or LU); justification for the proposed ATP; the full title of the method, company identification number and date of preparation of the proposed method; a complete description of the proposed method and of the approved method if used in a comparison; and the comparability data. All information provided to the Government is subject to the requirements of the Freedom of Information Act. Any proprietary information in the proposed method should be marked as "Confidential". USEPA staff will handle all proprietary information according to the regulations in subparts A and B of Part 2 of Title 40 CFR.

Initially an applicant should forward the above information, except the comparability data, to NERL-Cincinnati. Upon receipt of the application, the NERL-Cincinnati ATP staff will assign the application an identification number, which should be used in all future communications. The NERL-Cincinnati ATP staff will perform an initial evaluation of the submitted information and advise the applicant of the specific comparability data requirements, if applicable.

Method Description Requirements

Each method description must include the following topics, listed in the recently formulated Environmental Monitoring Management Council (EMMC) method format:

1.0 Scope and Application

Include analyte identification; CAS number; sample type; method sensitivity, expressed as mass; and, concentration range.

The concentration range of the proposed method should be equal to or greater than that of the approved method. If the range is smaller than that of the approved method (particularly, if the detection limit is higher), EMSL may advise that the method is inapplicable or the method may require a declaration of method limitations.

2.0 Summary of the Method

Describe the scientific basis, e.g., chemical principles, reactions, kinetics.

3.0 Definitions

4.0 Interferences

As a separate document, include data observed by applicant (during method development) using typical wastewater samples containing a specific quantity of an interfering substance.

5.0 Safety

Refer to good laboratory practice, appropriate material safety data sheets, and use of hood, goggles, and/or protective clothing. Emphasize any special procedure.

6.0 Equipment and Supplies

As a separate document, include any applicable manuals.

7.0 Reagents and Standards

Describe reagent formulations and shelf life of packaged materials.

8.0 Sample Collection, Preservation, Shipment, and Storage

The guidance in Table II of Part 136.3 of Title 40 of CFR takes precedence over the information published in the approved methods.

9.0 Quality Control

Indicate need for a formal laboratory quality control program; initial and periodic demonstration of performance by analyzing reagent blanks, check standards, and/or fortified samples; and maintenance of records, QC charts, etc. The periodic checking of performance should preferably occur at a minimum frequency of 10% of the total samples.

10.0 Calibration and Standardization

This section should include the calibration steps that are not performed daily. Include the daily calibration step(s) in the procedural section.

11.0 Procedure

Include in the method write up the procedural steps and the daily calibration steps. As a separate document include a typical calibration graph or curve.

12.0 Data Analysis and Calculations

13.0 Method Performance

Indicate the percent recovery, precision, and bias of the method for typical wastewater samples, fortified with known amount(s) of the analyte. Include the method detection limits (MDL), derived as outlined in Appendix B of section 136 of Title 40 of CFR, and expressed in weight/ volume. The calculated MDL should be confirmed by analyzing a sample at the calculated MDL concentration. Note that the MDL should be equal to or smaller than that of the approved method. If the MDL is higher, EMSL may advise that the method is inapplicable or the method may require a declaration of the method's limited range of performance.

14.0 Pollution Prevention

Cite good laboratory practices for pollution prevention.

15.0 Waste Management

Cite how waste and samples are to be disposed.

16.0 References

Include reference to documents and publications.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Any proprietary information in the proposed method should be marked "Confidential". USEPA staff will handle all proprietary information according to the regulations in subparts A and B of Part 2 of Title 40 of CFR.

If the proposed method is very similar to an approved and promulgated method, the applicant should simply prepare a two-column comparison of the approved and proposed methods. (The combined width of the two columns shall not exceed 17 inches.) This document should include the title and identification number of each method, the date of the proposed method and all the topics listed in the previous outline. The applicant should highlight any

differences in the proposed method. If the method is an automation of a previously approved manual method, any differences in kinetics and interferences should be presented and a comparison of the final ratios of the concentrations of the reactants in the proposed and approved methods should be included. This information should then be forwarded to NERL-Cincinnatii for review and recommendation regarding the comparability of the proposed method or need for an ATP application.

Comparability Data Requirements

A method comparability study will be required for each new or significantly revised method submitted for nationwide approval. Guidance for the comparability study is provided in the following text. Applicants are encouraged to have a brief consultation with the EMSL ATP staff regarding specific comparability study plans which may include the number of analyses, concentration levels, quality control activities, performance evaluation samples, etc. If a major area differs, such as the concentration range of the proposed method differs from that of the approved method, the applicant must consult with the NERL-Cincinnati ATP staff to determine the appropriate modification of the comparability study design.

The comparability data shall include observations of effluent samples, quality control samples in reagent water and performance evaluation samples in reagent water. Initially, each collected effluent will be analyzed once by the approved method to determine the concentration of the constituent of interest and the need for sample dilution and/or fortifying to achieve a baseline concentration equal to 5 times the method detection limit as detailed in the Subsample Preparation Requirements (pp. 7-8). After appropriate preparation, the subsamples of each effluent are to be analyzed by both the approved and proposed methods.

The quality control samples (QC) and the performance evaluation samples (PE) are to be prepared in reagent water and used to determine if the laboratory is in control. PE samples containing known analytes, but of concentrations unknown to the analyst, will be provided by EMSL along with instructions for use. The analyst is responsible for preparing the final QC and PE sample solutions for analyses. The QC and PE solutions must be spaced every tenth sample among the effluent samples which are to be analyzed by both methods.

As general guidance, the minimum number of analyses required are summarized in the following table. However, depending on the particulars of the method under review, the number of analyses may

change. We strongly suggest consultation with the EMSL ATP staff prior to analyses.

Type of Approval	Applicant	Initial Screening	Lowest Conc.*	Fortified	QC/PE	Total
Nationwide	Any	10	60	120-180	18-24	208-274
Limited Use	USEPA Regional, State or commercial	5	30	60-90	9-12	104-137
Limited Use	Individual	5	20	40	6	71

* It is highly desirable to use effluents which have a low level (5 x MDL) of the analyte(s) of interest. When this is not possible, the effluent must be diluted to a low level so that the fortified concentration is detectable and quantifible.

Effluent Sampling Requirements

For each constituent of interest, the applicant must collect a specified number of samples from a specified number of companies from a specified number of industry types, the latter identified by their individual 1987 Standard Industrial Classification (SIC) codes. The general requirements are summarized in the table below. Consultation with the EMSL ATP staff may result in changes to the general requirements based upon specific conditions of the method under review.

Approval type	Applicant	No. SIC codes	No. companies per SIC code	No. effluent samples per company	Total no. of samples
NW	Any	5	2	1	10
LU	USEPA regional, state, or commercial lab	5	1	1	5
LU	Individual discharger	1	1	5	5

The NERL-Cincinnati ATP staff will provide the appropriate constituent or analyte code(s) and 1987 SIC Codes and code descriptions to an applicant for either of the first two types of approval (listed above). If the applicant has difficulty locating appropriate sample sources (for these two types of applications), he may obtain (for a fee) a list of major companies, their addresses, contact persons, telephone numbers, and recent constituent measurements by directing a Freedom of Information (FOI) request to Jeralene B. Green, FOI Officer, MS-A101, 401 M Street, S.W., Washington, DC 20460, telephone: 202-260-4048. The requestor must designate the Permit Compliance System as the source of the information and specify the constituent or analyte code and name, the SIC codes, and geographical locations of interest (nationwide, regional, and/or state). Note that the individual discharger LU applicant must collect five samples of his own effluent, representing only one SIC code. Occasionally, an individual discharger may have two or more different effluents. In this case he should consult with the NERL-Cincinnati ATP staff concerning the sampling requirements.

An applicant is required to diligently select a source and/or time of collection that will afford a constituent concentration as close as possible to 5 x MDL. (If the MDL is unpublished, determine as directed in Section 13, Method Performance on p. 4.) This selection will enable the preparation of the required subsamples by either dilution or fortifying with a minimum of alteration of sample matrix.

All samples should be collected using the containers, preservation techniques, and holding times outlined in Table II of section 136 of the aforementioned CFR.

Subsample Preparation Requirements

The bias, precision and percent recovery of the proposed method will be compared to the bias, precision and percent recovery of the approved method. Several levels of concentrations covering the performance range of the proposed method will be used in the study. Ideally, the range of concentration for the proposed method will be the same as the approved method. This issue must be addressed with the EMSL ATP staff prior to analyses.

The study design initially requires a single analysis of each of the collected samples by the approved method to determine the concentration of the constituents of interest. If the initial concentration of the constituents in any collected sample differ from the 5 x MDL level, the sample must then be either carefully diluted or fortified to achieve the 5 x MDL level. Dilutions must be done using reagent water, as defined in the approved method. Sample fortifying must be accomplished using a substance whose character reflects the nature of the analyte in the effluents

and/or the calibration standards. For example, in an ATP for mercury the fortifying substance must consist of a mixture of inorganic and organic mercury compounds. Sample adjustment to the baseline or 5 x MDL concentration must be performed before splitting the sample into subsamples otherwise, the analytical error of each analysis may also include the error of any individual adjustment of the subsamples to the 5 x MDL level. Record and report all sample dilutions and/or fortifying required to adjust each sample concentration to the 5 x MDL level.

The fortifying of each subsample must also be achieved before aliquoting for analysis. Otherwise, the analytical error will include individual fortifying errors and the analytical data may be inappropriate. Record and report the amount of the substance added to each fortified subsample and the theoretical total concentration in each subsample. The latter is calculated for each subsample by adding the mean of the replicate analyses of the subsample by the approved method to the amount of substance added to that subsample. The evaluation of the comparability of the proposed method is dependent upon subsamples with very similiar concentrations.

Laboratory Requirements

It is highly desirable to have one laboratory analyze all the samples required in the study design. This is to eliminate the effects of multiple laboratories on the comparision of data between methods. Analyses by an additional laboratory should be included as a check but these data are in addition to the required ATP comparative analyses by the primary laboratory. This option should be discussed with the ATP staff prior to generating data. In nationwide applications, the laboratory should be independent, that is, without a vested interest in the company. NERL-Cincinnati will judge on the appropriateness of the suggested laboratory.

Approved Method Selection Requirements

Since the approval of an ATP depends upon the comparability of the proposed method to that of an approved method, the applicant's analyses by the approved method must also be examined to determine their acceptability as a basis in the comparison. This acceptability will be determined by comparing the applicant's analyses of QC and PE Samples by both the approved method and the proposed method.

The criteria used in the evaluation will be derived from available regulations, text of the approved method, and/or various interlaboratory validation and/or performance evaluation studies. USEPA may, consequently, limit the applicant's choice of an approved method to insure that the approved method used in a comparability study is one which has been evaluated with sufficient frequency in the interlaboratory studies to afford an appropriate

data base with which to determine the acceptability of the applicant's analyses by the approved method.

Effluent Subsample Analysis Requirements

Applicants for nationwide approval and individual USEPA Regional, State, or commercial laboratory applicants for limited-use approval of an ATP must perform six analyses of each subsample, three by the approved method and three by the proposed method. Individual dischargers applying for limited-use approval must perform four analyses of each subsample, two by the approved method and two by the proposed method. The effluent sample, effluent subsample, and analysis requirements (without screening analyses) are summarized in the following table:

Appvl.	Applicant	No. of collected samples	No. of sub-samples per collected sample	Total No. sub-samples for analysis	No. of replicate analyses per sub-sample per <u>each</u> of two methods	Total No. of analyses
NW	Any	10	3-4	30-40	3	180-240
LU	USEPA regional, State, or commercial lab	5	3-4	15-20	3	90-120
LU	Individual discharger	5	3	15	2	60

The aforementioned quality control analyses must be performed at a 10% frequency among the analyses of the effluent samples and subsamples (See Comparability Data Requirements, pp.5-6).

Data Reporting Requirements

Initial single observations of the collected samples by the approved method, dilutions and/or fortifying of each collected sample, the quantity of substance added to each subsample, and the total theoretical concentration of each subsample, the replicate observations of all subsamples by both methods, and quality control observations must be forwarded to USEPA.

A suggested format for reporting the observations of each set of subsamples is attached. The quality assurance observations associated with each set of subsample observations should also be tabulated and identified. An evaluation of the ATP application can be accomplished more quickly by the NERL-Cincinnati ATP staff if the information is also forwarded on one or more floppy discs compatible with an IBM-PC computer. The text on the disc should be presented in the latest version of Wordperfect (currently, 6.0) and the data may be presented in Wordperfect or in ASCII.

DATA REVIEW AND METHOD RECOMMENDATION

Upon receipt of an the applicant's data sets, NERL-Cincinnati staff will initiate its technical and statistical reviews. Appropriate criteria, derived either from published regulations or from interlaboratory studies, will be used to determine the acceptability of the approved method data as a basis in the evaluation of the analyses by the proposed method. If this evaluation is favorable, the evaluation of the comparability of the proposed method will follow.

Since the sampling and analytical requirements for each ATP application are based on a factorial experimental design with three factors, namely, method, sample matrix, and constituent concentration, each comparability review will be conducted over the range of these three factors. Descriptive statistics, such as the mean, standard deviation, coefficient of variation (relative standard deviation), and percent recovery of each set of replicates will be calculated. The precision of the proposed method will be compared with that of the approved method by means of a nonparametric statistical procedure attributable to Scheffe. An analysis of variance (ANOVA) will be used to compare the accuracy of the proposed method with that of the approved method.

Upon completion of the technical and statistical reviews, NERL-Cincinnati will prepare its recommendation for approval/disapproval, notify the applicant of its recommendation, and forward the recommendation to the appropriate approval authority. An ATP recommended for nationwide approval will be forwarded to the 304(h) Committee, which has been delegated the responsibility of proposing the ATP in the Federal Register.

After a three-month public comment period, this committee will review any submitted comments and prepare the final nationwide approval/disapproval decision and notice in the Federal Register. A recommendation for approval/disapproval of a limited-use ATP will be forwarded initially to the appropriate EPA Regional Administrator and, subsequently, to the appropriate State Agency Director, who are responsible for the final decision and notice to the applicant.

If you have any questions regarding the requirements, especially the comparability study design and the subsample fortifying, please contact the ENERL-CincinnatiCincinnati ATP staff at 513-569-7307.

REFERENCES

1. Villa, O. and L. Reed, Co-Chairs, EMMC Methods Integration Panel. Final Version of Approved EMMC Format (Memorandum to Members of EMMC Steering Committee, Methods Integration Panel, and Work Group, Tri-Chairs). U. S. Environmental Protection Agency, February 14, 1992, pp. 1-2.

Application No:_____ (USEPA Assigned)*

NPDES COMPARABILITY STUDY DATA

Source or Discharger Identity:_____

SIC Code:_____

Constituent Identity: _____

Concentration Units (weight/volume): _____

Initial Sample Constituent Conc. (Before Adjustment)_____

Initial Sample Adjustment
by Dilution_____ or by Fortifying_____
(specify) (specify weight/volume)

	Theoretical Conc.		Approved Method Observations			Proposed Method Observations		
Sub-samp	Amount Added*	Total Conc +	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
1	0							
2								
3								
4								

* Identify the applicant or source of data ONLY by the USEPA-assigned application number.
+ See pp. 7-8 of the protocol for a discussion of how these concentrations are derived.